Electrostatic and electrosteric stabilization of aqueous slips of 3Y–ZrO$_2$ powder

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Abstract

Yttria-doped zirconia powder (3Y-ZrO$_2$) was characterized and dispersed in distilled water. The state of dispersion was evaluated in terms of zeta potential, apparent viscosity and the mean particle size of solid phase in the slip. Zeta potential, apparent viscosity and the mean particle size as a function of pH indicated the pH range of electrostatic stabilization. These results showed that electrostatic stabilization of the slip can be accomplished in low acidic and high basic range of pH. Dissolution of yttria from the powder surface in acidic pH was found to be high and fast, risky to the stability of the slip as well as the microstructure of the sintered body. Electrosteric stabilisation by addition of an anionic polyelectrolyte (PMAA-NH$_3$) shifted the isoelectric point (IEP) to lower pH. The state of dispersion was further investigated by particle size measurements of the solid phase in the slip. The optimum amount of dispersant is discussed in terms of zeta potential and viscosity. The adsorption of polyelectrolyte is considered at pH 4, native pH of suspension and at pH 10, below and above the IEP of powder and correlated with the dissociation rate of polymer and the net surface charge of particles at given pH. Higher adsorption of dissociated polymer to the positively charged surfaces justifies the higher optimum amount of polyelectrolyte at pH 4. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical properties; Rheology; Slip casting; ZrO$_2$

1. Introduction

Yttria-doped zirconia has attracted attention due to its exceptional mechanical properties.[1–3] Wet colloidal processing techniques such as slip casting, tape casting, centrifugal casting and dip coating are employed to produce structural ceramics of improved reliability. Each of these processes requires a specific rheological behavior according to casting conditions.[4] The dispersion of the powder in a solvent can be achieved by the adjustment of the surface charge in electrostatic stabilization. The steric stabilization of a dispersion is achieved when polymer molecules attach to the surface of particles and prevent the mutual approach of the individual particles.

Rheology of partially stabilized zirconia has been discussed in many of the previous works[5] regarding the stabilization,[6] milling[7] and slip casting[8] processes. Despite the good knowledge of stabilization mechanisms[9] and the methods to make a well dispersed and stable slip, there is no general stabilization technique applicable for all 3Y–ZrO$_2$ powders. The powder properties, either chemical or physical can vary significantly depending on powder processing methods.[10]

In this study the rheology of a 3Y–ZrO$_2$ powder was investigated in order to find out a suitable stabilization method. The option to engage electrostatic stabilization was discussed taking into account the dissolution of yttria in the aqueous nitric acid solution. The steric stabilization of the slip was evaluated based on the fraction of dissociated polymer and the net surface charge of particles.

2. Materials and experimental procedures

3Y–ZrO$_2$ powder (HSY3) was supplied by Zirconia Mandoval UK. Specific surface area was characterized by the BET method using N$_2$ adsorption at temperature of liquid nitrogen −196°C (DeSorb/FlowSorb II 2300A, Micromeritics, USA). Sample was degassed at 200°C for half an hour before the measurement. Bulk chemical composition was measured by X-ray fluorescence and the most important constituents are illustrated in Table 1. The particle shape was studied by SEM (Philips SEM

Table 1
Properties of 3Y–ZrO$_2$ powder

Specific surface area (m^2/g)	6.9
Particle size, d_{50} (μm)	0.4[a]
Crystallite size (nm)	100[a]
Shape, particle size distribution	Spherical, monomodal[a]
Phase composition	26% m-ZrO$_2$, 74% t-ZrO$_2$
ZrO$_2$ (wt%)	92.6
Y$_2$O$_3$ (wt%)	4.5
SiO$_2$ (wt%)	0.1

[a] Data from the supplier. The balance in chemical composition is other oxides and minor elements that are not discussed in the paper.

515) and the phase composition was measured by X-ray diffraction technique using CuK$_\alpha$ radiation (Siemens D500, Germany). The polyelectrolyte dispersant (Darvan C, R. T. Vanderbilt, USA), used in the preparation of slips was the ammonium salt of polymethacrylic acid (PMAA-NH$_3$) containing 25 wt% active substance and 75 wt% water, with a molecular weight of 12000. The pH of the PMAA solution is 8.5.

Electrokinetic properties (zeta potential) and particle size as a function of pH were determined using electro-acoustic analysis (AcoustoSizer, Matec Applied Sciences, Hopkinton, MA, USA). The powder was dispersed (0.02 vol%) ultrasonically in 220 ml deionized water at room temperature and 10^{-2} mol NaCl was used as electrolyte to enhance the signals. At this solid loading the relation between the electrokinetic sonic amplitude (ESA) signal and the dynamic electrophoretic mobility was linear. The sizes of the particle were determined in parallel for the same suspensions.

The flow properties of the suspensions were measured at room temperature using a concentric cone and plate rotational rheometer (Bohlin visco 88 BV). Powder was added to distilled and deionized water and the pH was adjusted by adding nitric acid (10^{-1} M) or sodium hydroxide (10^{-1} M) in 1 h intervals during milling. The slurries were prepared by ball milling at room temperature for 4 h before the viscosity measurements. Aqueous slurry and grinding media, aluminosilicate balls, were charged at 50 vol% in a polyethylene container and 60 rpm rotational speed was applied. The viscosity values were taken for 50 and 75 wt% slurries, at a shear rate of 200 s^{-1} in which viscosity showed a stable trend in the Newtonian range. The 50 and 75 wt% slurries were prepared for slip spraying and slip casting, respectively. The reported concentrations of polyelectrolyte are given as weight percent of dry powder. All the measurements were performed at room temperature. Inductively coupled plasma emission spectroscopy (Perkin–Elmer ICP 2000) was used for the elemental analysis of the supernatant. For the solubility test, a 50 wt% slurry was prepared and pH was adjusted by nitric acid to 2 ± 0.1 in 50 ml suspension. The suspensions were stirred continuously in separate containers for the periods of 3, 10

and 110 h, and then centrifuged for 40 min at 3500 rpm. The clear supernatants were filtered and placed in sealed polymer bottles before the elemental analysis.

3. Results and discussion

One of the widely practiced methods to stabilize the slips is electrostatic stabilization, achieved by the repulsion of equally charged particles. The repulsive interaction results from the development of an electric double layer around the particles upon dispersing a powder into a polar media and is a function of pH, the concentration of specifically adsorbed ions and the ionic strength of the suspension.[11] The repulsive force decreases with increasing separation between the particles. The possibility and efficiency of electrostatic stabilization can be evaluated by measuring the zeta potential as a function of pH. The isoelectric point (IEP) of the powder, equals the pH at which the net surface charge of a particle is zero.

The particle surface is positively charged at pH < IEP and negatively charged at pH > IEP. The effect of pH on the zeta potential and mean particle size of the powder in the slurry as a function of pH is shown in Fig. 1. The IEP of the powder is at pH = 7.6. The zeta potential increases with increasing double layer thickness and with the total surface charge of the particle.[12] It is well known that the suspension stability is related to high zeta potentials.

When the IEP is approached from both sides, flocculation occurs as a result of lower surface charge densities. The mean particle size shows accordingly lower values in acidic and basic solutions and a weak peak around the IEP. The agglomerate size at pH around IEP is however not much bigger than the particle size in dispersed state (Fig. 1) due to the low solid loading in the experiment. Electrostatic stabilization of the slip was found to be efficient at acidic pH < 4 where zeta potential is over 40 mV.

A fine particle size, close to the primary particle size of powder, is associated with a fully dispersed suspension. The mean particle sizes of powder in dispersed suspension are lower than that given by supplier in Table 1.
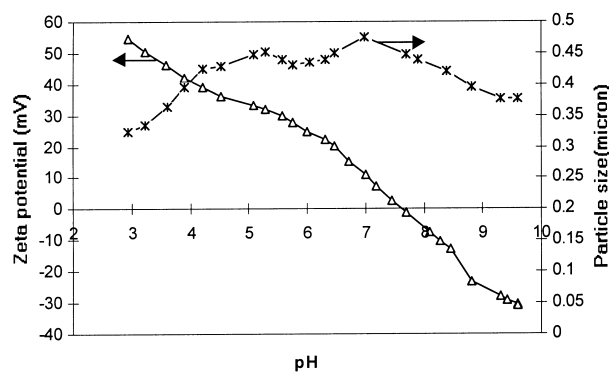

Fig. 1. Zeta potential and particle size of 3Y–ZrO$_2$ powder in aqueous suspension as a function of pH.

Since the disintegration of particles to finer sizes by sonication is unlikely, particle size of the lot used for zeta potential measurements must have been lower than the average size of powder in that batch. Furthermore the state of dispersion or flocculation can be evaluated by viscosity. Low viscosity is correlated to a high zeta potential. The measured viscosity of the suspensions as a function of pH and increasing solid concentrations are shown in Fig. 2.

Two pH ranges are characterized with a low viscosity. As the isoelectric point was approached either from acidic or basic pH, the viscosity increased rapidly and went beyond the range of the rotational viscometer, indicating a flocculation of the suspension. Apparent viscosities are almost the same in the acidic and basic range of pH at 50 wt% solid content. The increase in powder concentration, resulted in a viscosity increase at all other pHs except in the basic pH range 9.5–11. The lowest viscosity was obtained in basic pH above 9.5. However in zeta potential test, the highest zeta potential was found at 4.5 pH units below IEP while the measurement in basic pH was only extended up to 2 pH units above the IEP. The disagreement between the results of zeta potential and the apparent viscosity at acidic pH-range of dispersion indicates the possibility of yttria dissolution at low acidic pH.

Yttria is highly basic and prone to dissolve in acidic solutions. The dissolution of yttria influences the rheology of the suspension as well as the final microstructure of ceramic. Therefore it is important to know the level and kinetics of yttria dissolution in acidic solution. Yttrium ion Y^{+3} is the major species leached out, in the aqueous acidic media at pH = 2–7.[13] The chemical stability of some other tetragonal yttria doped zirconia powders has shown that yttria dissolves when the powders are suspended in HCl solutions.[14] Low surface area and high sintering temperature is in favor of lower solubility of yttria in acid solutions.[14] In colloidal processing, the amount and rate of dissolution of ions is important.[15] As shown in Fig. 3a, dissolution of yttrium is significant from HSY3 powder, but reaches a plateau after 10 h. Dissolution of Zr is lower than that of Si and

is slightly reduced with increasing mixing time (Fig. 3b). It is not clear whether the plateau in Fig 3a characterizes the equilibrium limit of the dissoluted ions or if the ions leached out to the solution are successively readsorbed on the surface.

The dominant Y^{3+} ion species, at acid pH values compresses the diffuse layer that is strongly influenced by the presence of multivalent ions.[16] When dissolution results in formation of multivalent Y^{3+}, the stability of suspension may thus be strongly affected. According to the Schulze–Hardy rule a concentration of 0.01–0.1 mmol/l of a trivalent cation is sufficient to fully compress the electrical double layer around the dispersed particles.[17] This explains the disagreement between the results of zeta potential and viscosity measurements in acidic range of pH and also the increase in viscosity with increase in solid load. In zeta potential test solid load is low and particles are exposed to acid media for a short time, whereas in viscosity measurements higher solid load slips were prepared after about 5 h treatment in acidic media.

There are other limits for electrostatic stabilization. Electrostatic stabilization of a highly concentrated slip is difficult, due to the short pH range of stabilization and the risk of flocculation with a small change of pH. At high concentrations of counter ions, the double layer is compressed and the particles come so close to each other
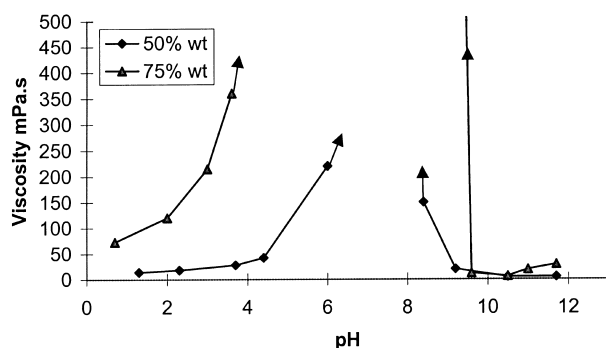
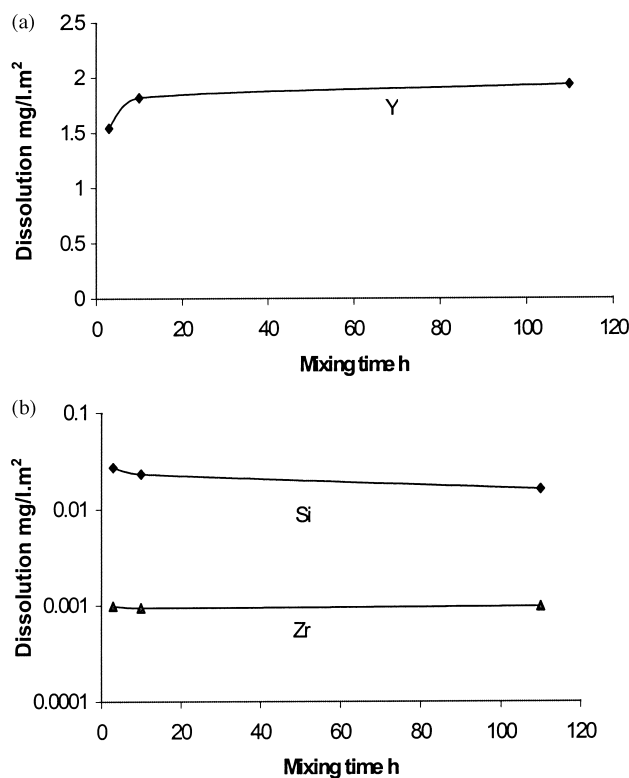Fig. 2. Viscosity vs. pH for different solid loading of 50 and 75 wt%.

Fig. 3. Dissolution of Y (a) and Si and Zr (b) in aqueous solution of nitric acid (pH 2) as a function of mixing time for 3, 10 and 110 h (values are normalized based on the unit surface area of the powder, note the different dissolution scales in a and b plots).
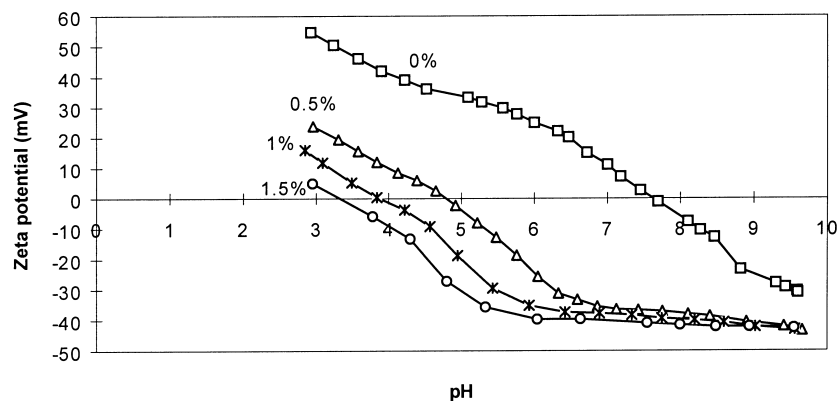
Fig. 4. Zeta potential as a function of pH for different addition of dispersant (PMAA) given in wt% of dry powder.

that there is a risk for attraction due to van der Waals forces. On the other hand a high concentration of acids is corrosive and attacks the mold used for casting, which can cause contamination by dissolution of gypsum.[18]

Due to the problems involved in electrostatic stabilization, polyelectrolytes are widely used in industrial applications. Anionic polyelectrolytes such as polymethacrylic acids (PMAA) are frequently used to disperse oxide particles.[19] Polymers adsorb on the particles and prevent the approach of the particles. Sterically stabilized suspensions can be thermodynamically stable while the electrostatically stabilized suspensions are only metastable. The ammonium polymethacrylate PMAA-NH_3 used in this study is an anionic polyelectrolyte. The dissociation reaction of PMAA-NH_3 creates free carboxylic acid groups that can be neutral COOH or dissociated to COO^-.[20] The pK_a (intrinsic acidity constant) of PMAA is at pH = 3–5. Depending on the solvent conditions, pH and ionic strength, the fraction of functional groups dissociated (COO^-) and nondissociated (COOH) will vary. The fraction of dissociated groups increases as the pH increases from acidic pH to basic pH. As the degree of dissociation increases the polymer charge varies from relatively neutral to highly negative. Fig. 4 shows the zeta potential as a function of pH for different amounts of dispersant added. The adsorption of anionic dispersant onto the surface of particle changed the net positive charge to negative charge and shifted the IEP to lower pH values.

The negatively charged PMAA adsorbs to the particle surface, enhances the negative potential and reverses the charge. The isoelectric point of the powder changed from pH 7.6 to 3.4 as a result of polyelectrolyte addition to the suspension up to 1.5 wt%. The higher negative zeta potential at pH > IEP means that PMAA has influenced the double layer build up and provided an electrosteric stabilization. At acidic pH < IEP, negatively charged PMAA neutralizes the positive sites of the surface and lowers the positive zeta potential values.

It is important to stabilize the slip with a minimum amount of polymer, since the excessive polymer has detrimental effect on the final ceramic products. The zeta potential at pH 7.6 (the IEP of suspension without polyelectrolyte) and the IEP as a function of dispersant added, are shown in Fig. 5. A large change towards negative zeta potential values was found by adding 0.5 wt% PMAA but insignificant changes with further addition of polyelectrolyte. This suggests that the adsorption has reached a saturation point. Also, a large decrease in the IEP (about 3 pH units) and zeta potential was shown when 0.5 wt% PMAA was added to the suspension, but further addition of polyelectrolyte shifted the IEP and zeta potential only moderately. Adding polyelectrolyte more than 0.5 wt% does not provide further increase in negative zeta potential and higher stabilization. The addition of 0.5 and 1% PMAA to a 50 wt% suspension shifts the pH to 8.5 and 8.7, which is in the pH range of high negative zeta potential and the small changes in pH, can not change the state of dispersion.

The mean particle size of the suspensions with the same amount of dispersant added is shown in Fig. 6. In the basic region a drop in the mean particle size was obtained by adding 0.5 wt% dispersant. Further addi-
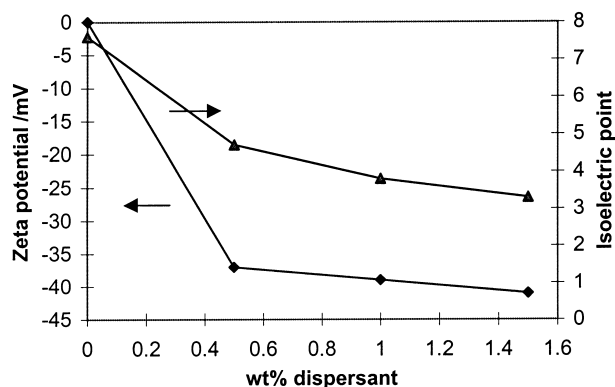

Fig. 5. Zeta potential at pH 7.6 (IEP of HSY3 suspension without dispersant) and isoelectric point (IEP) as a function of wt% dispersant (PMAA).

tion of dispersant up to 1.5 wt% had no effect on particle size in basic region of pH above 8. The addition of dispersant increased the agglomerate size in acidic suspensions below pH 4, indicating flocculation. The shift of IEP with addition of dispersant can be seen as a shift of the particle size peaks to lower pH (marked with arrows in Fig. 6).

Generally, the optimum concentration of dispersant is correlated with the minimum viscosity of the suspension. The optimum amount of dispersant depends on the net surface charge of particles and the fraction of dissociated groups as well as charge of the polymer. Moreover, the relative size of the polymer and the particle influences the effect of the polymer adsorption.

At a given pH, the adsorption saturation limit of the polyelectrolyte depends on the available sites for adsorption of the dissociated groups on the particle surfaces and on the charge density of the polymer. The affinity of the dissociated polyelectrolyte to the particle surface depends on the net surface charge of the particles and polyelectrolyte. It has been shown that the carboxyl groups adsorb in increasing amount on the surface of oxide ceramics as the pH of the suspension is lowered from IEP.[20] Dissociated polymer adsorbs to the surface, changes the surface charge and above a given surface coverage provides stabilization. Viscosity of the

suspensions were measured as a function of added polyelectrolyte at pH 4, i.e. below the IEP of powder, in which net surface charge of particles is positive, at native pH 8.5, i.e. above the IEP, in which net surface charge is slightly negative and at pH 10, in which the net surface charge is highly negative (Fig. 7). At pH 4, the adsorption saturation limit is high. The positively charged surface adsorbs more negatively charged, dissociated PMAA but at this pH, the dissociation rate of PMAA is low ($pK_a = 3–5$) and as a result higher amount of electrolyte is required to provide the stabilization. Therefore the lowest viscosity was obtained at higher amount of polyelectrolyte. The increase in viscosity at pH 4 at low amount of polyelectrolyte is probably due to the bridging flocculation effect. The same rheological observation has been reported on $3Y-ZrO_2$ suspension stabilized by PAA dispersant with a low surface coverage of polymer.[22] At low amount, negatively charged polymer chains were adsorbed to more than one positively charged particle surface thus forming bridges between particles. In the present case (at pH 4) the lowest viscosity was obtained at 1 wt% of PMAA. The competitive adsorption of the dissolved Y^{+3} ions on dissociated PMAA in the solvent at pH 4, nutralizes the charge and also contributes to the shortage of PMAA to attach to the particle surface.
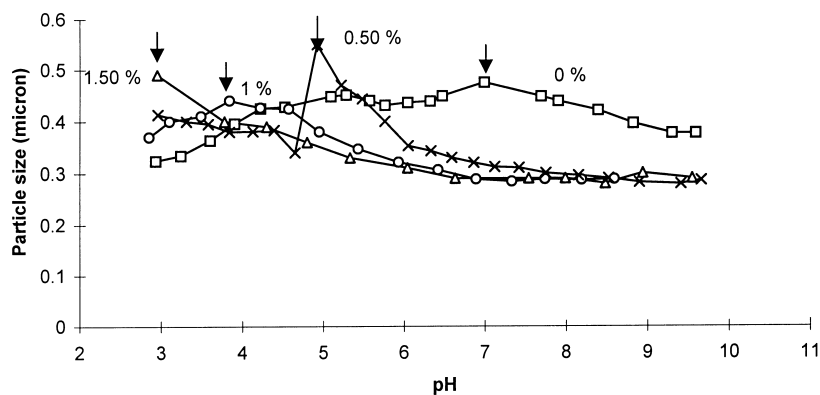

Fig. 6. Particle size of the solid phase in the suspension as a function of pH and concentration of dispersant. Particle size peaks are marked.
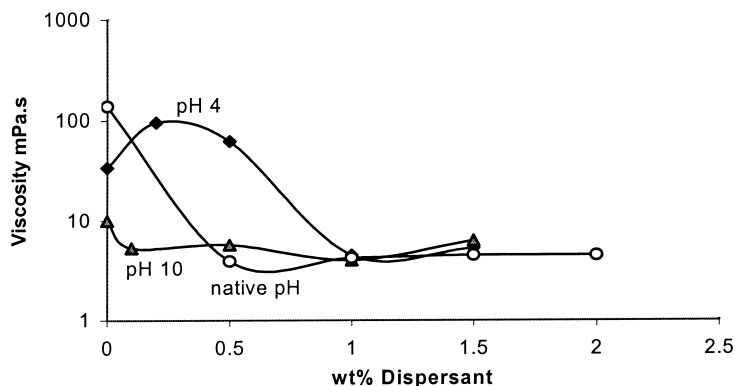

Fig. 7. Viscosity as a function of polyelectrolyte added at pH 4, native pH (8.5) and pH 10 (50 wt% solid loading).

At native pH (8.5), the particle surface being slightly negative, the saturation limit of minimum viscosity is around 0.5 wt%. The fraction of dissociated groups of PMAA is higher at this pH and despite the small potential repulsion a considerable enhancement of the negative zeta potential was found due to the adsorption of PMAA. At pH 10, particles have a highly negative net charge, the fraction of dissociated PMAA is the highest and adsorption takes place on the minority of positive sites on particles. The saturation limit of PMAA at pH 10 is low due to the low number of positively charged sites on the particle. Therefore the minimum viscosity is achieved with 0.1 wt% of PMAA at pH 10. Despite the low viscosity of suspensions at pH 10, a shear thickening behavior represented the possibility of coagulation as the shear rate increased. At this pH steric stabilization is provided via partial and random coverage of the surface by polymer chains due to the low number of positive sites on the particle surface, available for polymer attachment. It is suggested that, increase in the shear rate causes coagulation of particles and results an increase in viscosity. At higher amount of polymer there is no difference in viscosity at pH 4 and 10. With a further increase of polymer the viscosity increased.

At highly basic pH, in which the fraction of dissociated PMAA is high, the polymer chain is protruding into the solvent due to the enhanced stiffness. As the pH decreases, the dissociation decreases and the polymer chains are looped and more entangled.[21] Associated changes are expected in the adsorbed polyelectrolyte on the particle surface that changes the effective hydrodynamic radii of the particles.[19] When the polyelectrolyte adsorbs in a flat configuration, the stabilization is mainly electrostatic since the polymeric repulsion is short-range. With a thicker adsorbed layer, having chains protruding into the solution, the steric polymer contribution will become more important. Since the adsorption of highly charged polyelectrolyte on a weakly charged, amphoteric oxide surface usually results in an increase of the net surface charge density, the stabilization is electrosteric.[22] In the light of this understanding, electrosteric stabilization is suggested for the slurries at pH 8.5 and 10. These effects may become more important when the solid concentration increases or when the adsorbed molecular weight of polymer increases.

The viscosity of suspensions with 75 wt% solid loading, at native pH (8.5), as a function of dispersant is shown in Fig. 8. The minimum viscosity was obtained with addition of 0.9 wt% PMAA to a 75% wt suspension, which is higher than 0.5 wt% PMAA, found to obtain minimum viscosity of a 50 wt% suspension. The pH values after adding 0.9 wt% dispersant was 8.7. For concentrated slips, the optimum concentration of polyelectrolyte to ensure the stability of suspension is
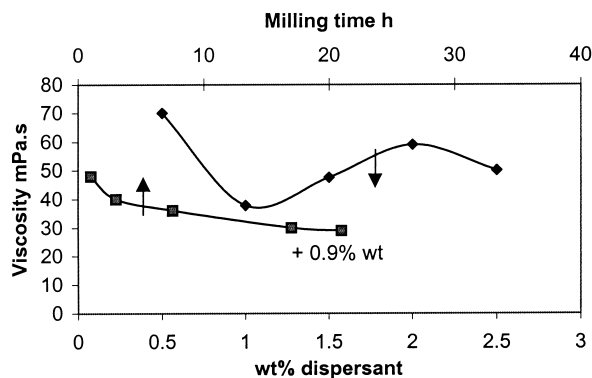

Fig. 8. Viscosity as a function of dispersant (for 4 h milling time) and milling time for 75 wt% solid loading suspension at native pH (8.5) with addition of 0.9 wt% PMAA.

higher than that determined by zeta potential in diluted slurry.

The increase in viscosity with a further addition of dispersant in Fig. 8 is due to the higher viscosity of the water solution containing free polyelectrolyte in a stretched conformation. When the possible sites for polymer adsorption are consumed, further addition of polyelectrolyte does not adsorb to the surface. The free polyelectrolyte, screens the effective charge on the particles and enhances the van der Waals attractive forces, and as a result increases the viscosity.[23]

Milling of the suspension with 0.9 wt%, the optimum concentration of polyelectrolyte up to 22 h lowered the viscosity moderately.

4. Conclusion

Electrostatic stabilization of aqueous yttria doped zirconia suspension was studied. In acidic pH-range the criteria of a low viscosity and a high zeta potential was initially fulfilled. Dissolution of yttrium ions in nitric acid solution of low pH was however significant up to 10 h mixing of the slip. The state of dispersion in the acidic suspensions was deteriorated due to the dissolution of yttrium ions that compress the double layer. The risk of coagulation in concentrated slips due to small changes in pH, makes electrostatic stabilization at acidic pH unreliable for slip casting techniques.

Adsorption of the polyelectrolyte (PMAA-NH$_3$) on the particle surface shifted the IEP to lower pH and increased the negative zeta potential in a large range of pH above the IEP. A minimum of 0.5 wt% PMAA shifted the IEP about 3 pH units towards lower pH values. Further addition of dispersant shifted IEP to lower pH only slightly, without increasing the zeta potential at pH > IEP.

The adsorption of PMAA was correlated to the net surface charge of the particles and the fraction of dissociated polymer at pH 4, 8.5 and 10, which is around and

above the pK_a of PMAA. At pH 4, below the IEP of the powder, the fraction of negatively charged dissociated polymer is low and has a high affinity to the positively charged particles. Adsorption of dissociated polymer on more than one particle at this pH, when added in quantities less than those required for stabilization resulted in an increase in viscosity due to bridging flocculation. A higher amount of polymer required for dispersion at acidic pH was due to higher adsorption of negatively charged polymer chains to the positively charged particles and the low fraction of dissociated groups available at acidic pH. At basic pH, above the IEP of the powder, the fraction of dissociated polymer increased but the surface charge of particles turned to be highly negative. As a result the lowest viscosity was obtained with only a small amount of PMAA. The optimum amount of polymer decreased as the pH of the slurry increased.

Acknowledgement

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